

4

DTIC FILE COPY

CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

CRDEC-TR-199

AD-A224 161

ESTIMATION OF LIQUID HEAT CAPACITIES
I. REVIEW AND EVALUATION OF MISSENARD METHOD

Elwin C. Penski

RESEARCH DIRECTORATE

June 1990

DTIC
ELECTE
JUL 25 1990
S & B D



U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

90 07 23 106

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

Distribution Statement

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1990 June		3. REPORT TYPE AND DATES COVERED Final, 88 Nov - 89 Dec	
4. TITLE AND SUBTITLE Estimation of Liquid Heat Capacities I. Review and Evaluation of Missenard Method				5. FUNDING NUMBERS PR-1C162622A553I	
6. AUTHOR(S) Penski, Elwin C.				8. PERFORMING ORGANIZATION REPORT NUMBER CRDEC-TR-199	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) CDR, CRDEC, ATTN: SMCCR-RSC-P, APG, MD 21010-5423				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This report uses Missenard group contribution values to calculate heat capacities of 10 compounds for comparison with measured literature values. Comparisons are also made with Kopp's rule. Good agreement between literature and calculated values is obtained with the Missenard group contribution method. Group contribution values and the details of the calculations are provided. <i>Keywords:</i>					
14. SUBJECT TERMS Liquid Group contributions, Kopp's rule, Heat capacity, Thermodynamics, Temperature. — (continued on reverse)				15. NUMBER OF PAGES 23	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	
				20. LIMITATION OF ABSTRACT UL	

14. Subject Terms (Continued)

t-Butyl amine	Diethyl malonate
→ Chloroethane	Diethyl sulfide
Diethyl disulfide	2-Methyl-2-propanol
Cyclohexane	2-Propyl amine

PREFACE

The work described in this report was authorized under Project No. 1C162622A553I, CB Simulants, Survivability, and Systems Science. This work was started in November 1988 and completed in December 1989.

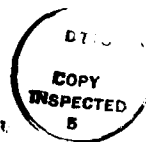
The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the Commander, U.S. Army Chemical Research, Development and Engineering Center (CRDEC), ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, Maryland 21010-5423. However, the Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for U.S. Government purposes.

This report has been approved for release to the public.

Acknowledgments

Special thanks are due to Donald Bowie and Dr. Kenneth Collins of the Research Directorate, CRDEC, for providing the computer system used to compose this report and to Donald Fielder and Ann Brozena, also of the Research Directorate, CRDEC, for providing technical comments. Thanks are also due to Corkey Smith and Patsy D'Eramo, Management Information Systems Directorate, CRDEC, for helping locate information.



Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Blank

CONTENTS

	Page
1. INTRODUCTION	7
2. BACKGROUND	7
3. CALCULATIONS	10
4. RESULTS	11
5. DISCUSSION	11
6. CONCLUSIONS	11
LITERATURE CITED	15
APPENDIXES	
A. DETAILS OF MISSENARD CALCULATIONS	17
B. KOPP'S RULE CALCULATIONS FOR LIQUIDS	23

Blank

ESTIMATION OF LIQUID HEAT CAPACITIES

I. REVIEW AND EVALUATION OF MISSENARD METHOD

1. INTRODUCTION

Many types of system analysis and design calculations are based on the thermodynamic properties of chemicals or materials. The thermodynamic properties of the chemicals or materials involved in any practical endeavor are part of the foundation of data required in every stage of planning, development, or analysis. Often, delays and problems result from not having a solid data foundation in place before starting a project. This investigation is one phase of an effort to build a data foundation for thermodynamic properties.

One of the most severe problems with developing satisfactory models to simulate the behavior of agents is the nonavailability of an adequate data base of physical chemical properties over a range of temperatures. Heat transfer kinetics, evaporation, rheology, decomposition, and temperatures resulting from many processes are critically dependent on heat capacity data.

This report is the first in a series of reports. The purpose of the series is to report calculations of heat capacities for a variety of types of compounds. One method is described in this report. Calculated values are compared with literature values for a few alcohols, amines, and other classes of compounds. The chemicals studied in this report (Table 1) were chosen on the basis of their relation to compounds of interest and the quality of the data available for each of them.

2. BACKGROUND

Heat capacity is defined as the heat absorbed for a degree rise in temperature per unit volume or mass.¹ If the process takes place at constant pressure, then

$$C_p = (\delta H / \delta T)_p \quad (1)$$

where

C_p = Heat capacity at constant pressure

H = Heat absorbed

T = Temperature

Table 1. Compound Names, Structures, and Molecular Weights

Compound Names	Structure	Molecular Weight
1-Amino-pentane, n-amyl amine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	87.164
2-Butanol, sec-butyl alcohol	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHOH} \\ \\ \text{CH}_3 \end{array}$	74.122
t-Butyl amine, 2-methyl-2-aminopropane	$(\text{CH}_3)_3\text{CNH}_2$	73.138
Chloroethane, ethyl chloride	$\text{CH}_3\text{CH}_2\text{Cl}$	64.515
Cyclohexane	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2-\text{CH}_2 \end{array}$	84.161
Diethyl disulfide, 3,4-dithiahexane, (DEDS)	$\text{CH}_3\text{CH}_2\text{SSCH}_2\text{CH}_3$	122.243
Diethyl malonate, (DEM)	$\text{CH}_2(\text{CO}_2\text{CH}_2\text{CH}_3)_2$	160.169
Diethyl sulfide, 3-thiapentane, (DES)	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$	90.183
2-Methyl-2-propanol, t-butyl alcohol	$(\text{CH}_3)_3\text{COH}$	74.122
2-Propyl amine, isopropylamine	$(\text{CH}_3)_2\text{CHNH}_2$	59.111

Over a narrow temperature range, the heat capacity of a liquid is often represented by the following equation:

$$C_p = a + bT + cT^2 \quad (2)$$

where a, b, and c are empirical constants. The equations for broad temperature ranges are much more complex.

Missenard² has developed a functional group method for calculating heat capacities for a few classes of organic liquids in the -25 to 100 °C range. The method involves adding group contributions in the following manner:

$$C_p = \sum_{i=1 \text{ to } m} n_i G_i \quad (3)$$

where

- i = number for each type of functional group, index
- m = total number of different functional groups in the compound
- n_i = number of times i-th type functional group is found in the compound
- G_i = value of group contribution for i-th type group

Table 2 provides the Missenard group contribution values used in this report. While there are other parameters, there are no parameters for organophosphorus compounds. The Missenard estimation method is not applicable to reduced temperatures* in excess of 0.75.

The units for heat capacity at constant pressure are traditionally calorie/(Kelvin mole). In this report the units are also given in the more practical units [calorie/(Kelvin kilogram)] where mass replaces mole. Kilograms are used for mass in order to fit the data more compactly into the tables. International units [joule/(Kelvin mole)] can be obtained by multiplying the traditional units by 4.1840.

* Reduced temperature is usually defined as the ratio of temperature to critical temperature in units of Kelvin.

Table 2. Liquid Heat Capacity Group Contribution Values from Missenard

		Liquid Heat Capacity Group Contribution Values cal/(mole K)					
		Temperature, °C					
Group	Index	-25°	0°	25°	50°	75°	100°
$\begin{array}{c} \\ -C- \\ \end{array}$	2	2.0	2.0	2.0	2.0	2.0	-
-Cl	7	6.9	7.0	7.1	7.2	7.35	7.5
-S-	10	8.9	9.0	9.2	9.4	-	-
$\begin{array}{c} \\ -CH- \end{array}$	11	5.0	5.7	5.95	6.15	6.35	6.7
-CH ₂ -	12	6.5	6.6	6.75	6.95	7.15	7.4
-CH ₃	13	9.2	9.55	9.95	10.4	10.95	11.55
-COO-	14	13.5	13.8	14.1	14.6	15.10	15.5
-OH	17	6.5	8.0	10.5	12.5	14.75	17.0
-NH ₂	19	14.0	14.0	15.0	16.0	-	-

Most of the literature values for heat capacity were taken from Domalski, Evans, and Hearing.³ Although more than one value was available in their collection, the value with the highest rating by the above authors was used.

3. CALCULATIONS

The calculations were performed with a pocket calculator and checked on an IBM PC, Version C1.10 computer in BASIC Language Version D2.10 using a program named MISS, which was written by the author.

4. RESULTS

Heat capacities of organic compounds obtained by the Missenard estimation method are compared with literature values in Table 3. The comparisons are within a few calories per mole per degree; or the average deviation is less than 5%. The blanks in the tables are where the Missenard parameters are not available. Table 4 lists the liquid heat capacity values from the Missenard estimation method in units of calorie/(kilogram Kelvin). Details of the calculations are given in Appendix A.

Kopp's rule¹ was also tested and included in Table 3. This rule produces errors of about 50% or larger in most cases. See Appendix B for details of the Kopp's rule calculations. Kopp's rule sums the contributions of elements; whereas the Missenard method sums the contributions of groups of elements.

5. DISCUSSION

The Missenard method appears to provide satisfactory heat capacities for alcohols, amines, chlorinated hydrocarbons, and esters. The disadvantages of the Missenard estimation method are that it is not applicable to reduced temperatures in excess of 0.75, and there are no group contribution parameters for organophosphorus compounds. The later problem stems from the fact that practically no experimental measurements of heat capacity for organophosphorus compounds have been made. Also at the temperatures above 25 °C, thus far, insufficient data was available for the chosen compounds to verify the Missenard system at temperatures above 25 °C.

6. CONCLUSIONS

The Missenard method appears to provide satisfactory heat capacities for alcohols, amines, chlorinated hydrocarbons, and esters. The average deviations between the measured values for the compounds selected for this study and values calculated by the Missenard method are less than 5% from -25 to 25 °C.

Table 4 provides calculated liquid heat capacities for 10 compounds from -25 to 100 °C.

Kopp's rule for the heat capacities of liquids gave values that deviated from measured values by about 50% at 25 °C.

Table 3. Summary and Comparison of Missenard Estimation and Kopp's Rule Values with Liquid Heat Capacity Measurements

Compound	Heat Capacity cal/(mole K)					Source
	Temperature, °C					
	-25°	0°	25°	50°	75°	
1-Amino-pentane	49.2	50.0	52.0 52.1 84.4	54.2	-	Estimate Measured ³ Kopp's Rule
2-Butanol	36.4	39.4	43.1 47.1	46.4	50.2	Estimate Measured ³
	36.8	41.3	46.9 65.2	53.3		Measured ⁴ Kopp's Rule
t-Butyl amine	43.6	44.7	46.9 45.9 72.0	49.2	-	Estimate Measured ³ Kopp's Rule
Chloroethane	22.6	23.2	23.8 26.0 37.6	24.6	25.5	Estimate Measured ³ Kopp's Rule
Cyclohexane	39.0	39.6	40.5 37.4 74.4	41.7	42.9	Estimate Measured ³ Kopp's Rule
Diethyl disulfide	49.2	50.3	51.8 48.8 74.0	53.5	-	Estimate Measured ³ Kopp's Rule
Diethyl malonate	64.9	66.5	68.4 68.1 101.2	70.95	73.6	Estimate Measured ³ at 21.4 °C Kopp's Rule
Diethyl sulfide	40.3	41.3	42.6 41.0	44.1	-	Estimate Measured ³
	38.8	39.8	40.6 66.6			Measured ⁵ Kopp's Rule
2-Methyl-2-propanol	36.1	38.6	42.3 45.3 65.2	45.7	49.6	Estimate Measured ³ Kopp's Rule
2-Propyl amine	37.4	38.8	40.85 39.1 59.6	42.95	-	Estimate Measured ³ Kopp's Rule

Table 4. Liquid Heat Capacity Values from Missenard Estimation Method in Units of Calorie/(Kilogram Kelvin)

Compound	Heat Capacity cal/(kg K)					
	Temperature, °C					
	-25°	0°	25°	50°	75°	100°
1-Amino-pentane	564	573	596	622	-	-
2-Butanol	491	532	581	626	677	731
t-Butyl amine	596	610	641	673	-	-
Chloroethane	350	359	369	381	394	410
Cyclohexane	463	471	481	495	501	528
Diethyl disulfide	402	411	424	438	-	-
Diethyl malonate	405	415	427	442	459	476
Diethyl sulfide	447	458	472	489	-	-
2-Methyl- 2-propanol	487	521	571	617	669	-
2-Propyl amine	633	656	691	727	-	-

Blank

LITERATURE CITED

1. Dean, J.A., Lange's Handbook of Chemistry, 13th ed., (pp 9-177), McGraw Hill Book Company, New York, NY, 1985.
2. Missenard, D.F., "Additive Method for Determining the Heat Capacities of Liquids," Comptes Rendus de L'Academie des Sciences Vol. 260, p 5521 (1965).
3. Domalski, E.S., Evans, W.H., and Hearing, E.D., "Heat Capacities and Entropies of Organic Compounds in the Condensed Phase," J. Phys. Chem. Ref. Data Vol. 13, Suppl. 1 (1984).
4. Andon, R.J.L., Connett, J.E., Counsell, J.F., Lees, E.B., and Marten, J.F., "Thermodynamic Properties of Organic Oxygen Compounds, Part XXVII. (+/-)-Butan-2-ol and (+)-Butan-2-ol," J. Chem. Soc. (London), Sec. A. Inorganic, Physical, and Theoretical Chem. No. 4, p 662 (1971).
5. Scott, D.W., Finke, H.L., Hubbard, W.N., McCullough, J.P., Oliver, G.D., Gross, M.E., Katz, C., Williamson, K.D., Waddington, G., and Huffman, H.M., "3-Thiapentane: Heat Capacity, Heats of Fusion, and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions," J. Am. Chem. Soc. Vol. 74, p 4656 (1952).

Blank

APPENDIX A

DETAILS OF MISSENARD CALCULATIONS

Table A-1. Calculation of Liquid Heat Capacities of 1-Amino-pentane

Group	n_i	Functional Group Contributions $\times n_i$ cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	1	9.2	9.55	9.95	10.4	10.95	11.55
-CH ₂ -	4	26.0	26.4	27.0	27.8	28.6	29.6
-NH ₂	1	14.	14.	15.	16.	-	-
Heat Capacities cal/(mol K)		49.2	49.95	51.95	54.2	-	-

Table A-2. Calculation of Liquid Heat Capacities of 2-Butanol

Group	n_i	Functional Group Contributions $\times n_i$ cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	2	18.4	19.1	19.9	20.8	21.9	23.1
-CH ₂ -	1	6.5	6.6	6.75	6.95	7.15	7.4
-CH- 	1	5.0	5.7	5.95	6.15	6.35	6.7
-OH	1	6.5	8.0	10.5	12.5	14.75	17.0
Heat Capacities cal/(mol K)		36.4	39.4	43.1	46.4	50.15	54.2

Table A-3. Calculation of Liquid Heat Capacities of t-Butyl Amine

Group	n_i	Functional Group Contributions x n_i cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	3	27.6	28.65	29.85	31.2	32.85	34.65
$\begin{array}{c} \\ -C- \\ \end{array}$	1	2.0	2.0	2.0	2.0	2.0	-
-NH ₂	1	14.	14.	15.	16.	-	-
Heat Capacities cal/(mol K)		43.6	44.65	46.85	49.2	-	-

Table A-4. Calculation of Liquid Heat Capacities of Chloroethane

Group	n_i	Functional Group Contributions x n_i cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	1	9.2	9.55	9.95	10.4	10.95	11.55
-CH ₂ -	1	6.5	6.6	6.75	6.95	7.15	7.4
-Cl	1	6.9	7.0	7.1	7.2	7.35	7.5
Heat Capacities cal/(mol K)		22.6	23.15	23.8	24.55	25.45	26.45

Table A-5. Calculation of Liquid Heat Capacities of Cyclohexane

Group	n_i	Functional Group Contributions $\times n_i$ cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₂ -	6	39.0	39.6	40.5	41.7	42.9	44.4
Heat Capacities cal/(mol K)		39.0	39.6	40.5	41.7	42.9	44.4

Table A-6. Calculation of Liquid Heat Capacities of Diethyl Disulfide

Group	n_i	Functional Group Contributions $\times n_i$ cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	2	18.4	19.1	19.9	20.8	21.9	23.1
-CH ₂ -	2	13.0	13.2	13.5	13.9	14.3	14.8
-S-	2	17.8	18.0	18.4	18.8	-	-
Heat Capacities cal/(mol K)		49.2	50.3	51.8	53.5	-	-

Table A-7. Calculation of Liquid Heat Capacities of Diethyl Malonate

Group	n_i	Functional Group Contributions $\times n_i$ cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	2	18.4	19.1	19.9	20.8	21.9	23.1
-CH ₂ -	3	19.5	19.8	20.25	20.85	21.45	22.2
-COO-	2	27.0	27.6	28.2	29.2	30.2	31.0
Heat Capacities cal/(mol K)		64.9	66.5	68.35	70.85	73.55	76.3

Table A-8. Calculation of Liquid Heat Capacities of Diethyl Sulfide

Group	n_i	Functional Group Contributions $\times n_i$ cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	2	18.4	19.1	19.9	20.8	21.9	23.1
-CH ₂ -	2	13.0	13.2	13.5	13.9	14.3	14.4
-S-	1	8.9	9.	9.2	9.4	-	-
Heat Capacities cal/(mol K)		40.3	41.3	42.6	44.1	-	-

Table A-9. Calculation of Liquid Heat Capacities of
2-Methyl-2-Propanol

Group	n_i	Functional Group Contributions x n_i cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	3	27.6	28.65	29.85	31.2	32.85	34.65
$\begin{array}{c} \\ -C- \\ \end{array}$	1	2.0	2.0	2.0	2.0	2.0	-
-OH	1	6.5	8.0	10.5	12.5	14.75	17.0
Heat Capacities cal/(mol K)		36.1	38.6	42.3	45.7	49.6	-

Table A-10. Calculation of Liquid Heat Capacities of
2-Propyl Amine

Group	n_i	Functional Group Contributions x n_i cal/(mol K)					
		Temperature, °C					
		-25°	0°	25°	50°	75°	100°
-CH ₃	2	18.4	19.1	19.9	20.8	21.9	23.1
$\begin{array}{c} -CH- \\ \end{array}$	1	5.0	5.7	5.95	6.15	6.35	6.7
-NH ₂	1	14.	14.	15.	16.	-	-
Heat Capacities cal/(mol K)		37.4	38.8	40.85	42.95	-	-

Blank

APPENDIX B

KOPP'S RULE CALCULATIONS FOR LIQUIDS

The following table shows the calculations for the Kopp's Rule heat capacities (cal/mole K), C_p , for liquids.*

Table. Kopp's Rule Calculations for Liquids

Compound	Atomic Heat Capacities Times the Number of Each Element						C _p
	Element						
	C	H	O	S	N	Cl	
1-Amino-pentane	5x2.8	+13x4.8	+ 0x6	+0x7.4	+ 1x8	+ 0x8	= 84.4
2-Butanol	4x2.8	+10x4.8	+ 1x6				= 65.2
t-Butyl amine	4x2.8	+11x4.8			+ 1x8		= 72.0
Chloroethane	2x2.8	+ 5x4.8				+ 1x8	= 37.6
Cyclohexane	6x2.8	+12x4.8					= 74.4
Diethyl disulfide	4x2.8	+10x4.8		+ 2x7.4			= 74.0
Diethyl malonate	7x2.8	+12x4.8	+ 4x6				=101.2
Diethyl sulfide	4x2.8	+10x4.8		+ 1x7.4			= 66.6
2-Methyl- 2-propanol	4x2.8	+10x4.8	+ 1x6				= 65.2
2-Propyl amine	3x2.8	+9x4.8			+ 1x8		= 59.6

*Dean, J.A., Lange's Handbook of Chemistry, 13th ed., (pp 9-177), McGraw Hill Book Company, New York, NY, 1985.